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LOW-TEMPERATURE SYNTHESIS OF GRANULAR GLASS FROM MIXES BASED ON SILICA-ALUMINA-CONTAINING COMPONENTS FOR OBTAINING FOAM MATERIALS

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It is established that granular glass can be obtained as an intermediate product for foam glass crystal materials based on common silica component (marshallite, diatomite, opoka) at temperatures not exceeding 900°C. It is shown that the use of granular glass with glass phase present in amounts greater than 80 wt.% makes it possible to obtain foam crystal glass materials with density up to 250 g/cm^3.

Key words: granular glass, marshallite, diatomite, opoka, low-temperature synthesis, foam glass crystal materials.

Ecologically safe and fireproof long-lived thermal insulation materials are now of practical interest in the construction industry. Foam glass materials meet all these requirements, but questions concerning expansion of the raw materials base for the production of such materials remain topical. There is a need to develop more readily accessible materials, for example, such as foam crystalline materials, which might be obtainable by a two-stage technology that includes synthesis of granular glass by means of low-temperature treatment of a mix with a certain composition (RF Patent No. 2326841).

The objective of our work is to establish the possibility of obtaining granular glass as an intermediate product for foam glass crystalline materials based on common silica components at temperatures not exceeding 900°C.

One condition for the formation of melt and a glass phase at relatively low temperatures is high dispersity of the main refractory components of the mix — silica. In a previous work we established that the silica size fraction is less than 100 μm [1]. The use of natural finely dispersed materials will expand the raw materials base for obtaining granular glass, since classic glassmaking is based on quartz sand with particle size 0.1 – 0.5 mm. To preserve the chemical uniformity of a finely dispersed mix during heat-treatment and to increase its chemical activity the mix was first densified by rolling in a dish-shaped granulator and a granular glass was obtained in the form of partially fused porous granules [2, 3].

In addition to a high dispersity of the refractory material, an important condition for synthesis of the granular glass is the composition of the initial mix, which is based on three components: high-silica glass former, alkali (fluxing addition), and alkaline-earth, which affects primarily the viscous properties of the melt. To determine the component composition of the mix, the phase diagrams of the three-component system Na_2O – CaO – SiO_2 were analyzed and a base composition was chosen for the glass. The concentration range of the glass was determined taking account of the following limiting requirements:

the amount of the glass formers in the composition must exhibit high stability with respect to glass formation; the silicon oxides content of the glass must be no lower than 60 and no higher than 75%[4];

the content of alkali metal oxide should be in the range 13 – 22%, for which a glassy state obtains after the melt cools;

the prescribed composition of the mix should lie near the boundary lines and eutectics, this corresponds to a lower melting temperature and the highest crystallization power of the melt;

the amount of melt should not be less than 70%, and its viscosity should be adequate for forming foam;

the mix should be heated to a temperature no higher than 900°C, which corresponds to our objective.

Analysis of the diagram showed that the following compositions satisfy these requirements (%): low-temperature eutectic of the system (melting temperature 725°C) 21.3 Na_2O, 5.2 CaO, 73.5 SiO_2 [4] and the composition on the

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[4] Here and below — content by weight unless otherwise stipulated.

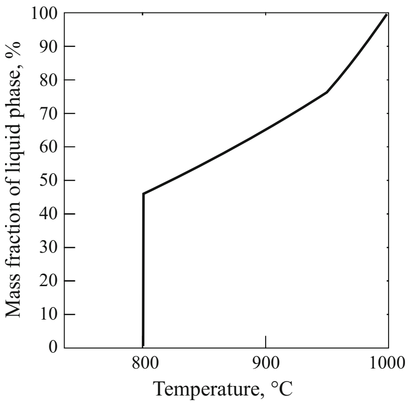

Fig. 1. Fusibility curve.

curve separating devitrite and silica (melting temperature about 950°C), which contains 16.0 Na_2O, 11.0 CaO, and 73.0 SiO_2. The limiting compositions chosen correspond to different ratios of the components and fall within the glass-formation region.

The calculations established that the fraction of the liquid phase formed, which is necessary to obtain granular glass, in the temperature interval 800 – 950°C is sufficient. It should be expected that real mix treatment temperatures will be lower because of the impurities present in the initial components. The variation of the melt fraction formed when mix with the second limiting composition is heated is reflected in Fig. 1 in the form of the fusibility curve.

It should be noted that the silica component of the mix must have a relatively high content of SiO_2 (at least 80%) in order to provide the required amount of melt and to obtain glass with the chosen composition. In addition, for cost-effectiveness the initial material should be quite widely available, inexpensive, and accessible. Silica rocks such as marshallite, diatomite, and opoka were investigated for this reason; their chemical composition (Table 1) is represented by a quite high content of SiO_2 and the presence of impurity oxides, which are not harmful because they are part of the composition of glass and are taken into account in the mix inventory. Because of their fineness marshallite, opoka, and diatomite have a high specific surface area — 5500, 2600, and 2300 cm^2/g, respectively.

Amorphous SiO_2 is present in the form of opal in dispersed silica rocks; depending on age and bedding conditions, opal metamorphizes into α-cristobalite and then into α-quartz. Materials such as diatomite and opoka consist mainly of opal-cristobalite-tridimite phases, whose determination is problematic because of the strong overlapping of the reflections in the powder diagrams. The interplanar distances of the strongest lines of different modifications of silica lie in a quite narrow range of angles: α-quartz (0.426 nm) — 20.835°, tridimite (0.474, 3.840 nm) — 20.350, 23.143°; cristobalite (0.404 nm) — 21.983°; opal (0.408 nm) — 21.765°. For this reason, a special computational procedure must be used make a comparative assessment of these materials.

A graphics editor and an analyzer of x-ray diffraction patterns — the Renex program, which is intended for analyzing the x-ray diffraction patterns with strongly overlapping reflections — were used in the present work. The structural parameters of the cristobalite, tridimite, quartz, and opal phases were used as initial models. As the description of the observed profile of the x-ray diffraction pattern is optimized, the parameters of the background component and the scale factors determining the content of the mineral components were varied. The x-ray diffraction patterns of opoka and diatomite as well as the result of their decomposition (Fig. 2) show that these materials are polyphase and consist of four phases.

Marshallite (powdered quartz), which is a monomineral crystal rock of sedimentary origin, is represented predominately by β-quartz and a negligible amount of kaolinite (Fig. 3).

In summary, the phase analysis (Table 2) shows that these silica materials can be arranged in the following order with increasing content of SiO_2 in them in the crystalline form: diatomite, opoka, and marshallite. Evidently, the highest treatment temperatures of the mixes at the granular glass production stage will be characteristic for mixes with marshallite and the lowest treatment temperatures will be characteristic for mixes with diatomite and opoka.

The component composition of the mix calculated according to the limiting compositions of the glass differs by the ratio of the main components and the nature of the glass-forming material, which determines the various temperature regimes of their treatment. For this reason, individual treatment and soaking temperatures were determined for each mix, and the content of the residual crystalline phase was chosen as the quality criterion for the granular glass. The component composition of the mix for obtaining granular glass based on silica initial material is presented in Table 3.

A comparative analysis of the amount of the crystalline phase of the granular glass was made using the XPA data to-

TABLE 1.

Material	Deposit	Content, wt.%					
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	other
Marshallite	Elbashenskoe	95.70	2.10	0.27	0.80	0.60	0.53
Diatomite	Inzenskoe	86.44	5.30	1.60	0.74	0.53	5.39
Opoka	〃	83.00	5.25	2.72	2.05	1.47	5.51

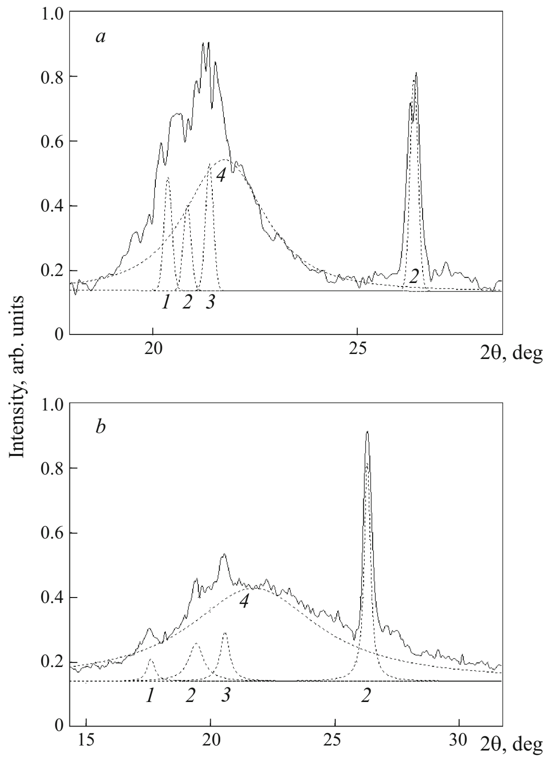

Fig. 2. X-ray diffraction patterns of opoka (*a*) and diatomite (*b*) and the result of their decomposition into phases: *1*) tridimite, *2*) quartz, *3*) cristobalite, *4*) x-ray amorphous opal.

gether with a calibration curve, which was constructed using an internal standard method. High-purity (99.9579%) Chupinskoe quartz, which possesses quite intense diffraction peaks of reflection, corresponding to β-quartz (d = 3.35 and 4.25 nm), was chosen as the reference standard. The calibration curve was constructed according to several standard mixtures, varying the quantity of the crystalline phase (quartz) in the glass from 8 to 16%. The intensity of the reflections of the standard was compared with that of the amorphous halo background of the diffraction pattern according to the relation

$$\Sigma I_c / I_b = \text{const } C_c ,$$

where I_c is the sum of the intensities of the diffraction reflection of the crystalline phase of the reference standard (0.335, 4.250 nm), arb. units; I_b is the intensity of the diffraction reflection of the amorphous halo, arb. units; and, C_c is the mass content of the crystalline phase, %.

The diffraction patterns of the reference standards of the mixtures are presented in Fig. 4, and the calibration curve calculated on their basis is presented in Fig. 5. As one can see, the dependence of $\Sigma I_c / I_b$ on the concentration of the crystalline phase in the glass is rectilinear, so that it can be used to determine the content of the crystalline phase of the granular glass.

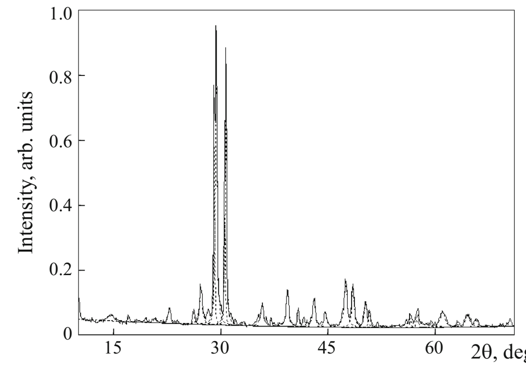

Fig. 3. X-ray diffraction pattern of marshallite.

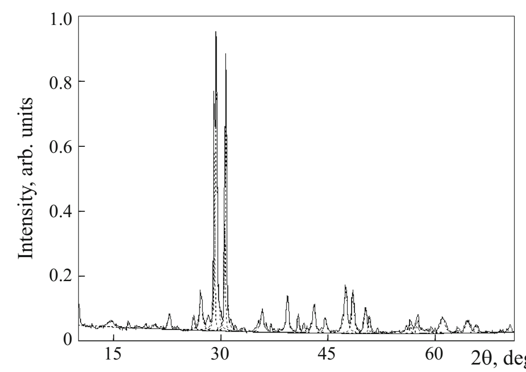

Fig. 4. X-ray diffraction pattern of glass with quartz content (wt.%): 8 (*1*), 10 (*2*), 12 (*3*), 14 (*4*), and 16 (*5*).

TABLE 2.

Silica material	Phase content, vol.%		
	crystalline forms of silica	amorphous opal	other crystalline phase (including clayey)
Diatomite	14	70	16
Opoka	13	57	30
Marshallite	95	–	5

TABLE 3.

Mix*	Content, wt.%				
	soda	dolomite	marshallite	opoka	diatomite
M-1	30	7	63	–	–
M-2	20	17	63	–	–
D-1	27	6	–	–	67
D-2	18	16	–	–	66
O-1	29	3	–	68	–
O-2	17	15	–	68	–

* Marshallite mixes) M-1, M-2; diatomite mixes) D-1, D-2; opoka mixes) O-1, O-2.

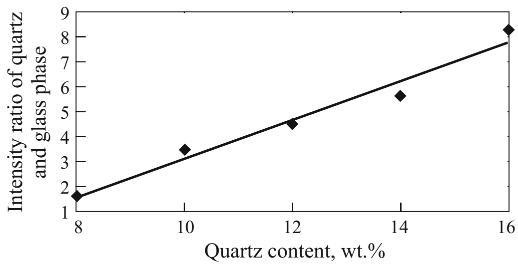

Fig. 5. Calibration curve for determining the content of the crystalline phase of the granular glass.

It was determined that the residual content of the crystals is 10 – 20%; the largest amount of glass phase is present in the granular glass based on diatomite and the lowest amount in marshallite. The mix is based on a material containing amorphous SiO_2 exhibits a higher chemical activity at the silicate- and glass-formation stages. As the amorphous fraction increases, the glass phase of the granular glass in the component increases.

As the mix processing temperature increases, the content of the crystalline phase decreases in all compositions. When diatomite and opoka are used the decrease is observed to 850°C with subsequent stabilization of the amount of residual quartz. Evidently, this is due to the relatively low softening temperature of the mix and the early appearance of a high-viscosity liquid phase, which has a wedging effect and degrades the dissolution of the crystalline SiO_2. For mixes with marshallite, the glass-formation process at temperatures to 900°C does not proceed in the entire volume; for this reason it is recommended that the mix be processed at higher temperatures or additional preparation of the mixture by mechanical activation be used.

In summary, finely dispersed silica material can be used as a component in the mix to obtain a granular glass at relatively low temperatures taking account of the following factors:

granular glass with glass-phase content greater than 80% makes it possible to obtain a foam glass crystalline material with density to 250 g/cm^3, strength 3 MPa, and water absorption to 6%;

the amount of the glass phase in the granular glass increases with increasing fraction of the amorphous component in the silica component of the mix.

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